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In-situ X-ray Diffraction Studies of the Dehydration of Zinc-Exchanged Zeolite A.

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Introduction: There have been previous reports of a rhombohedral phase of Na-A. Recent studies into the dehydration process of zinc-exchanged zeolite A have also shown the presence of a cubic to rhombohedral phase transition [1]. Upon further heating, a second phase transition occurred resulting in a high temperature cubic phase. The previous studies on Zn-A were carried out by dehydrating Zn-A at certain temperatures and packing the samples into glass capillaries, therefore little information was obtained about the nature and kinetics of the phase transition. There have been 2 theories of the origin of the rhombohedral phase transition seen in Na-A. Bursill et al. suggested that the rhombohedral distortion was due to a change in the silicon/aluminum ordering in the zeolite framework [2]. While Bennett et al. suggested that ordering of the charge balancing cations caused the phase transition [3]. In-situ diffraction studies were performed on Zn-A to provide information on the dehydration mechanism and the nature of the rhombohedral phase formed and to test these 2 possible suggestions.

Methods and Materials: Zinc-exchanged zeolite A was produced from the sodium form by conventional aqueous ion-exchange methods. A small amount of the sample was packed into a sapphire capillary and nitrogen gas was flowed over the sample in order to remove any water vapor given off as the sample was heated. The sample was heated from room temperature to 650°C using a temperature ramp of 2°C/min and diffraction patterns were collected every 6 minutes. A wavelength of 0.9276Å was used.

Results: The results show that the phase from cubic to rhombohedral occurs at approximately 150°C, while the second phase transition back to cubic crystal symmetry occurs at approximately 600°C. The results also show that the changes are gradual, as the diffraction patterns around the transition temperatures are clearly a mixture of the two phases.

Conclusions: The nature of the phase changes observed indicate that a change in the ordering of the framework silicon and aluminum atoms to produce the rhombohedral phase is unlikely as these atoms would have to re-arrange once more to form the high temperature cubic phase. Also, Löwensteins rule would be violated. Therefore, it is logical to conclude that it is the rearrangement of the charge balancing cations that is responsible for the rhombohedral distortion from cubic symmetry. Recent work by Kazansky et al [4] on ZnNa-Y showed that zinc-oxide or hydroxide clusters are formed during the initial stages of dehydration which subsequently break down at higher temperatures to give isolated Zn^{2+} cations coordinated to the zeolite framework. It is possible that a similar mechanism takes place here and further work is currently in progress to determine if any cluster species are formed.

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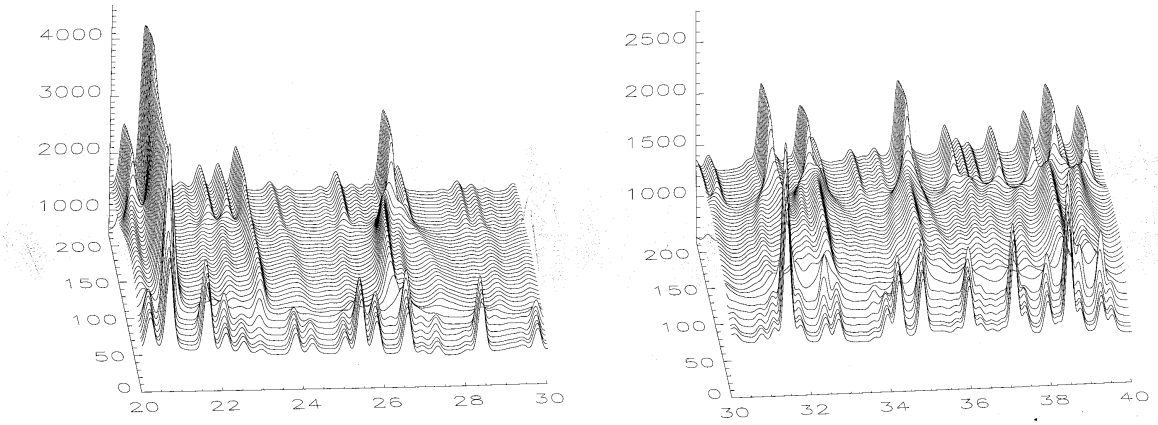

Figure 1: In-situ X-ray diffraction data of the dehydration process of zinc-exchanged zeolite A.